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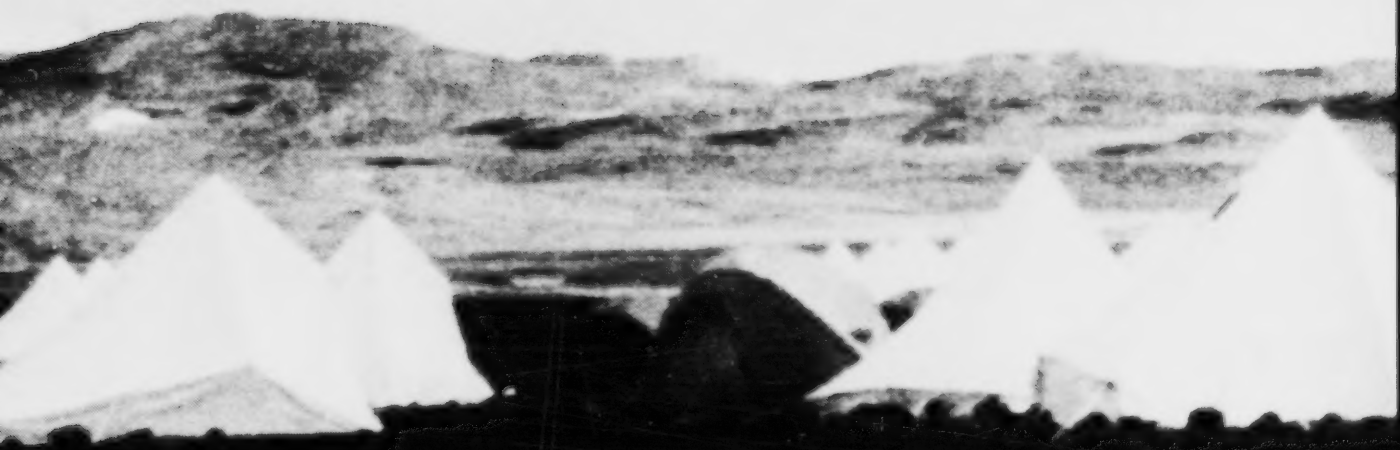
2002



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Author's address

J.J. Carroll *(jeff.carroll@gnb.ca)*
New Brunswick Department of Natural Resources and Energy
Geological Surveys Branch
P.O. Box 50
Bathurst, New Brunswick E2A 3Z1

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Lithogeochemistry of Ordovician sedimentary rocks associated with Ni-Co stream-silt anomalies along Ritchie Brook, Kedgwick map area, northern New Brunswick[1]

J.I. Carroll
GSC Quebec, Quebec

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Abstract: The Upper Ordovician Grog Brook Group is composed of 1) a lower siltstone-dominated unit, 2) a thin-bedded carbonaceous and sulphidic shale unit, and 3) an upper sandstone-dominated unit. In the north-central part of the map area, which is traversed by Ritchie Brook, these units are spatially associated with magnetic and Ni-Co stream-silt anomalies.

Twenty-one samples were collected along Ritchie Brook and analyzed for selected major and trace elements. The MnO content is higher in the sandstone-dominated unit than in the lower two units. Organic carbon content is greater within the lower two units, reflecting more reducing conditions and/or higher organic productivity at the time of deposition. The major-element content of the carbonaceous shale unit is indistinguishable from that of the siltstone-dominated unit. Although the carbonaceous shale is weakly 'metalliferous', it is not the source of the Ni and Co anomalies identified in the area. An unknown subjacent source is inferred.

Résumé : Le Groupe de Grog Brook (Ordovicien supérieur) est composé des unités suivantes : 1) une unité inférieure à dominance de siltstone, 2) une unité de minces lits de shale carbonacé et sulfureux et 3) une unité supérieure à dominance de grès. Dans la partie centre nord de la région cartographique, laquelle est traversée par le ruisseau Ritchie, ces unités sont spatialement associées à des anomalies magnétiques et des anomalies en Ni-Co de sédiments silteux de ruisseau.

Vingt et un échantillons ont été récoltés le long du ruisseau Ritchie et analysés pour des éléments majeurs et en traces spécifiques. Le contenu en MnO est plus élevé dans l'intervalle supérieur gréseux que dans les deux unités inférieures. La teneur en carbone organique est plus grande dans les deux unités inférieures, réflétant des conditions plus réductrices et/ou une plus grande productivité organique au temps de dépôt. Le contenu en éléments majeurs du shale carbonacé est indifférentiable de celui de l'unité à dominance de siltstone. Bien que le shale carbonacé soit faiblement métallifère, il n'est pas la source des anomalies en Ni et Co identifiées dans la région. La présence d'une source inconnue à faible profondeur est déduite.

[1] Project funded by the NATMAP Appalachian Foreland and Platform Architecture in Quebec, New Brunswick and Newfoundland: Contribution to the Geological Bridges of Eastern Canada.

INTRODUCTION

The Kedgwick map area, part of the Gaspé Belt (Fig. 1, 2), is host to a conspicuous regional magnetic anomaly and spatially associated Ni-Co stream-silt anomalies (Geological Survey of Canada, 1998a; Pronk and Frisk, 1999). Investigations have focused on determining if the geochemical anomalies are genetically related to this magnetic anomaly or to a stratigraphic source. The magnetic anomaly may reflect the presence of Middle Ordovician mafic and/or ultramafic volcanic rocks or alternatively, the anomaly may be attributed to mafic and/or felsic intrusions at depth, although no contact metamorphic aureole has been identified in the area. If the source of the geochemical anomaly is sedimentary, it may be related to carbonaceous black shale in the Upper Ordovician Grog Brook Group. To test the latter hypothesis, a lithogeochemical transect was carried out along Ritchie Brook, in the eastern part of Kedgwick map area.

The Ritchie Brook section provides relatively good exposure that transects the three new lithological subdivisions identified within the Grog Brook Group (St. Peter, 1978; Carroll, 2000). One of these units, a carbonaceous black shale, is particularly interesting as a stratigraphic source for the geochemical anomalies because of its relatively high sulphide and organic carbon contents, the latter of which commonly concentrates transition metals (Wignall, 1994; Arthur and Sageman, 1994). The objective of this study is to identify any geochemical variation among the Grog Brook lithotypes and to possibly identify any near-surface source(s) of the stream-silt geochemical anomalies. A determination of the 'metalliferous' character of the 'carbonaceous black shale' is attempted based on the proposed definition of Huyck (1991) in order to propose the unit as a possible source of the geochemical anomalies. This work constitutes part of the regional NATMAP bedrock-mapping program termed, 'Appalachian Foreland and St. Lawrence Platform Architecture in Québec, New Brunswick and Newfoundland' and concentrates on the southern extremity of NATMAP's transect #3 (Matane-Restigouche).

REGIONAL SETTING

The Gaspé Belt extends from the eastern part of the Gaspésie in Quebec through northwestern New Brunswick and into the northeastern part of the United States (Fig. 1) and constitutes a fore-arc successor basin that existed from the Late

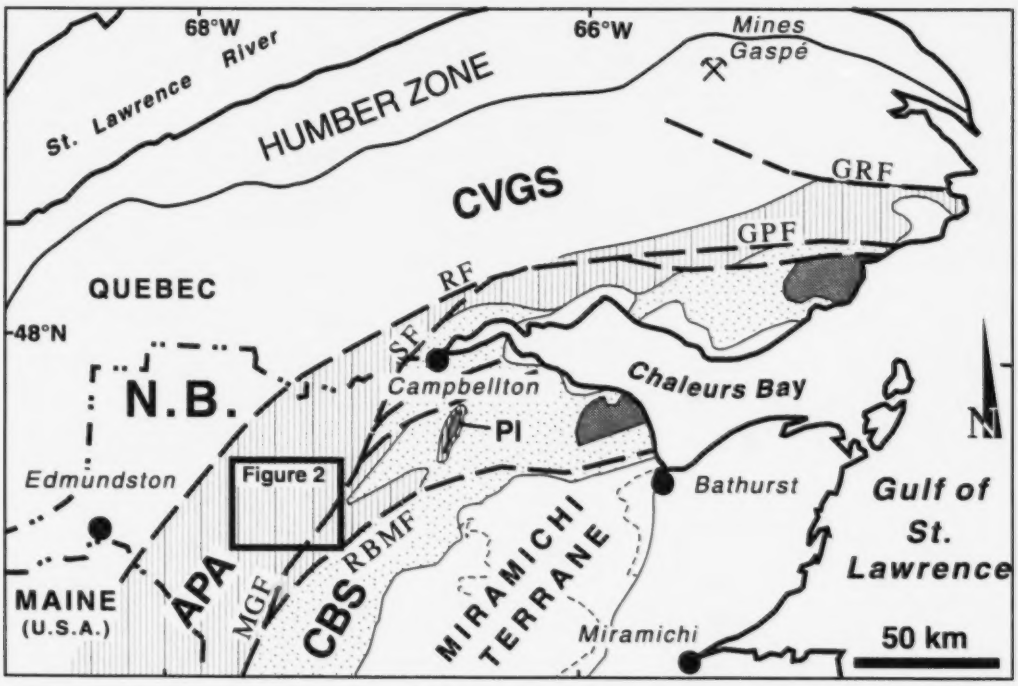

Figure 1. *Major geological zones of Gaspésie and northern New Brunswick showing the post-Taconian Connecticut Valley-Gaspé synclinorium (CVGS), the Aroostook-Percé anticlinorium (APA) (vertical hatching), and the Chaleurs Bay synclinorium (CBS) (stippled pattern). The NTS 21-O/11 map area is indicated by the bold block (expanded in Fig. 2). Regional faults are: RF=Restigouche Fault, GRF=Grande Rivière Fault, GPF=Grand Pabos Fault, SF=Sellarsville Fault, MGF=McKenzie Gulch Fault, RBMF = Rocky Brook-Millstream Fault. The Popelogan inlier (Dunnage Zone) is represented by PI.*

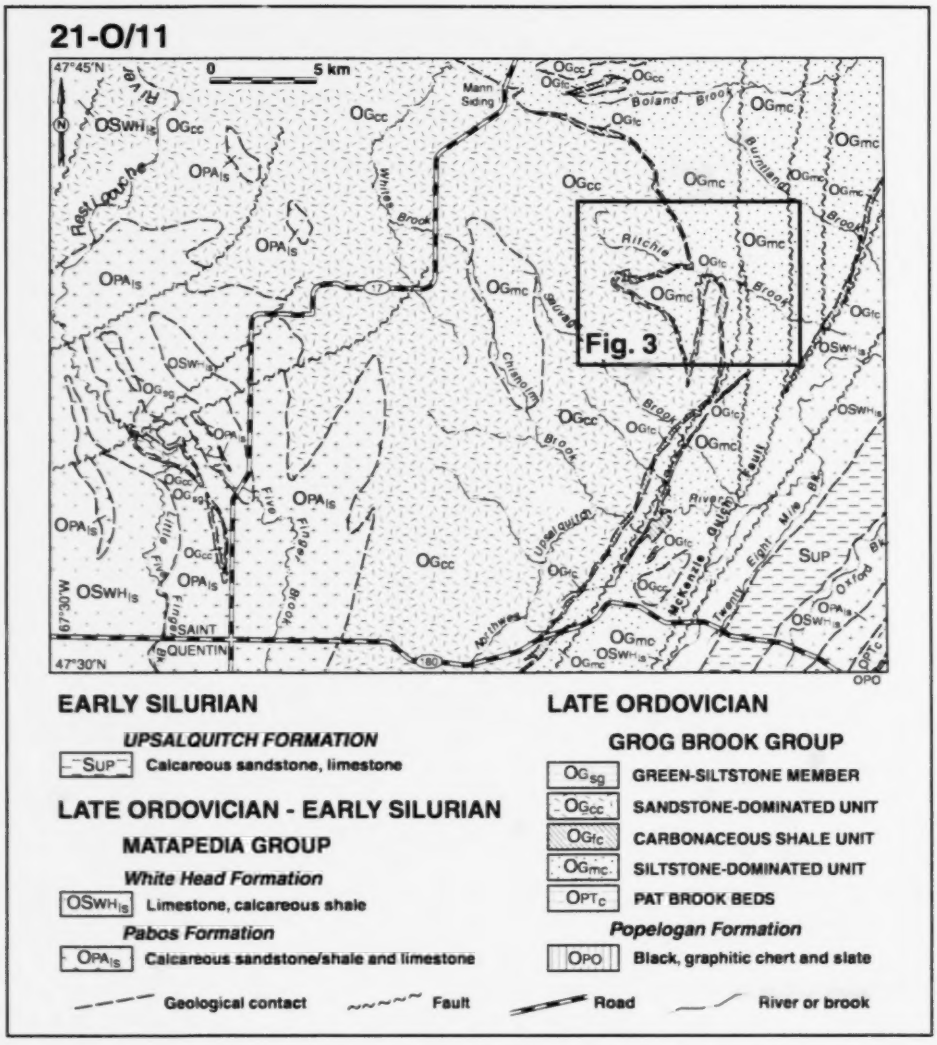

Figure 2. *Geological bedrock map of the NTS 21-O/11 map area. Study area (Fig. 3) is indicated by the bold inset box.*

Ordovician until the onset of the Early to Middle Devonian Acadian Orogeny (Malo and Bourque, 1993; Bourque et al., 1995). The basin is divided into three broad tectonostratigraphic domains (Fig. 1): the Chaleur Bay syclinorium, the Aroostook–Percé anticlinorium, and the Connecticut Valley–Gaspé synclinorium (Bourque et al., 1995). Upper Ordovician to lowermost Silurian rocks are confined to the Aroostook-Matapédia anticlinorium and consist of siliciclastic and calcareous rocks of the Grog Brook (Honorat Group in Quebec) and Matapedia groups, respectively (Fig. 2). The three tectonostratigraphic domains are interpreted to be conformable (St. Peter, 1978; Bourque et al., 1995) although, in northwestern New Brunswick, the western margin of the Aroostook–Percé anticlinorium is in fault contact with the uppermost Silurian–Lower Devonian rocks of the Connecticut Valley–Gaspé synclinorium along the Restigouche Fault. The eastern margin is both locally conformable and in fault contact with the Chaleur Bay syclinorium along the Rocky Brook–Millstream, McKenzie Gulch, and Sellarsville faults. Basement of the Gaspé Belt is interpreted to consist of Dunnage Zone rocks which, in New Brunswick, are represented by sediments and mafic volcanic rocks of the Popelogan Terrain (van Staal and de Roo, 1995).

LOCAL GEOLOGICAL SETTING

The eastern half of the NTS 21-O/11 map area is divisible into eastern and western domains that are separated by the north-northeasterly striking McKenzie Gulch Fault (Fig. 2).

Rocks of the Balmoral (Ordovician) and Matapédia (Upper Ordovician–lowermost Silurian) groups, and of the Upsalquitch Formation (Lower Silurian) underlie the eastern domain. West of the fault, rocks of the Upper Ordovician Grog Brook Group underlie the area (Fig. 2). The Ritchie Brook section is located in the western domain (Fig. 3) and is underlain by three new lithological subdivisions of the Grog Brook Group (Carroll, 2000). They are from oldest to youngest (east to west): 1) a siltstone-dominated unit; 2) a black, carbonaceous shale unit that conformably overlies the siltstone unit; and 3) an upper sandstone-dominated unit consisting of relatively coarse-grained sandstone and subordinate siltstone that may locally fill various-size channels crosscutting the previous two units. These rocks are interpreted to have been laid down in a deep marine slope — toe of a slope environment via contour, channel-fill, and overbank deposition.

Siltstone-dominated unit

The siltstone-dominated unit (OG_{mc} in Fig. 3) is the oldest unit in the succession. It consists of grey-black to dark grey, noncalcareous, thin- to medium-bedded (5–20 cm) siltstone, argillite, and shale with thin beds (2–10 cm) and laminae (1–5 mm) of fine-grained, dark grey to medium-dark grey, noncalcareous to weakly calcareous sandstone (Carroll, 2000). Mudrock facies make up 60–80% of the unit. Thin laminae (1–2 mm) of black carbonaceous material occur throughout the unit, but are only volumetrically significant near the contact with the overlying carbonaceous shale unit. The unit is thought to overlie mafic volcanic and sedimentary rocks of the Popelogan Terrain which is exposed approximately 25 km northeast of the study area.

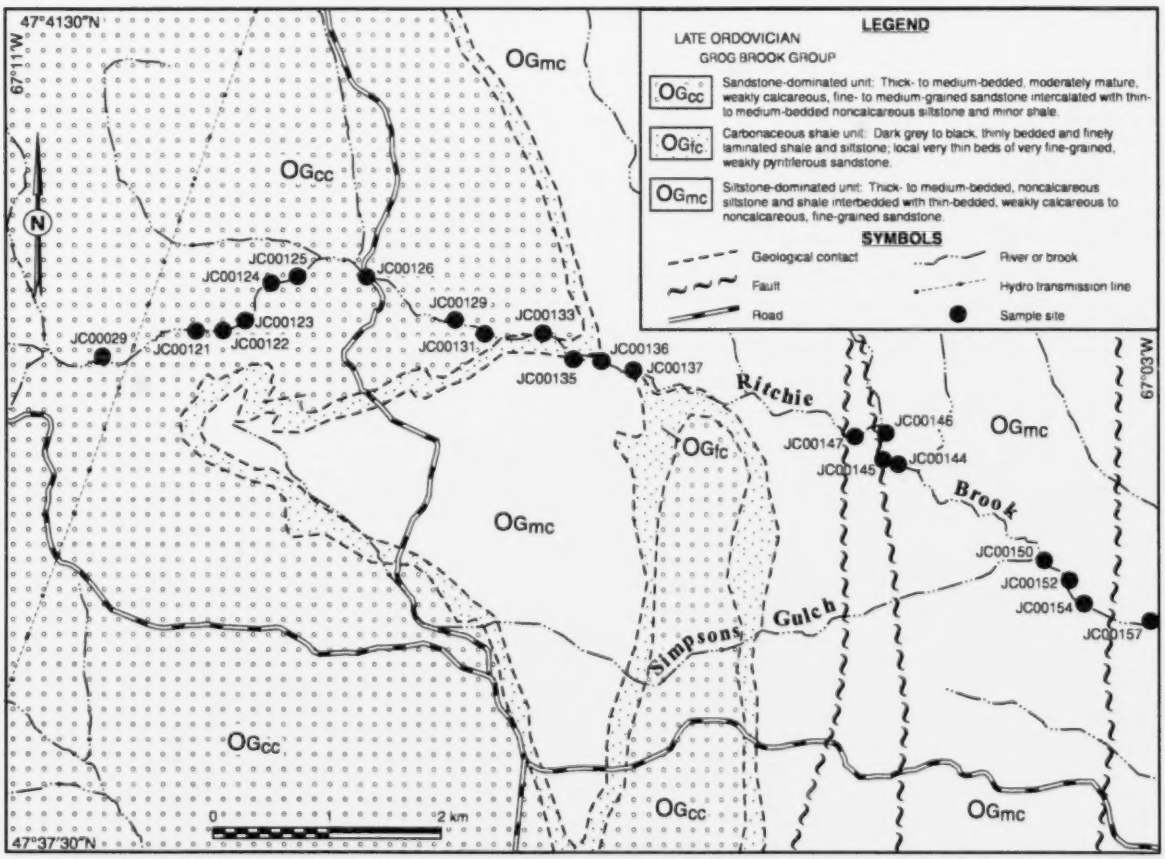

Figure 3. *Detailed geology of the study area (NTS 21-O/11 east) with the location of analyzed samples along Ritchie Brook.*

Carbonaceous shale unit

The carbonaceous shale unit (OG_{fc} in Fig. 3) conformably overlies the siltstone-dominated unit and consists of thin-bedded (0.5–2 cm) grey-black to dark grey, parallel laminated, nonbioturbated, very fine-grained sandstone and siltstone interbedded with thin-bedded (0.5–2 cm), black, carbonaceous, faintly laminated shale (Carroll, 2000). The transition from the siltstone-dominated unit to the carbonaceous shale is generally gradational over an interval ranging from 10 m to as much as 100 m; although it is relatively abrupt (~ 30 m) along Ritchie Brook. Visible pyrite is common within the lighter, very fine-grained sandstone and siltstone and commonly occurs on the same side of the individual beds adjacent to the carbonaceous layers, presumably indicating slightly coarser grain size near the base of the sandy layers.

Sandstone-dominated unit

The sandstone-dominated unit (OG_{cc} in Fig. 3) consists of fine- to medium-grained, light grey to medium grey, thin- to thick-bedded (10 cm to more than 25 cm), variously micaceous and weakly calcareous sandstone interbedded with dark to medium grey, noncalcareous siltstone and lesser shale (St. Peter, 1978; Carroll, 2000). Bedforms are typical of deposition by turbidity currents and locally display full Bouma sequences, although c to e intervals are most common. The siltstone in this unit is typically lighter grey than the one within the lower unit. Sandstone makes up approximately 60–75% of the unit, although along the Ritchie Brook transect, sandstone accounts for approximately 50% of the outcrop.

Intrusive rocks

Intrusive rocks in the area consist of felsic and mafic dykes and sills. The felsic dykes and/or sills are more abundant east of the McKenzie Gulch Fault and are typically emplaced parallel to it. They consist of pink to orange-pink, very fine-grained, variously porphyritic to aplitic rocks and are usually 2–20 m in thickness. Mafic dykes and/or sills predominate west of the fault and consist of dark green to grey-green, fine-grained, phaneritic and variously porphyritic rocks that are commonly oriented both parallel to the fault and in a north-south direction.

METHODS

A total of 21 samples were collected from the three units of the Grog Brook Group in order to represent the various lithotypes within these units as well as those areas where sulphide mineralization and fault structures were more apparent (Fig. 3). Ten samples of each the sandstone-dominated and the siltstone-dominated units and one sample of the carbonaceous shale unit were collected. Within the sandstone-dominated unit, six samples of sandstone and four of siltstone were taken. Within the siltstone-dominated unit, nine samples of siltstone and one of sandstone were collected.

The samples were analyzed by XRAL Laboratories of Don Mills, Ontario utilizing XRF spectrometry on fused disks for determination of major oxides and group I and II trace metals and INNA or ICP-MS for the rare-earth elements and transition metals. Milling was performed using an agate mill. Incomplete digestion precluded the evaluation of the REE data with the exception of sample JC000137, which was analyzed using a lithium metaborate-tetraborate fusion ICP process and was performed by Activation Laboratories Ltd. of Ancaster, Ontario. In the latter case, milling was performed using a mild steel mill. The analytical results are listed in Appendix 1. Analytical accuracy was evaluated using United States Geological Survey geochemical reference standard SDO-1 (Devonian Ohio Shale). All elements are within the recommended values with the exception of Ag, Au, W, Ta, Br, and Ge, which are in very low concentrations in the standard and are not well established (Fig. 4).

RESULTS

Sandstone-dominated unit

Figures 5 and 6 illustrate the variations in CaO, MnO, organic carbon (C org), and total C and S in an easterly oriented transect along Ritchie Brook. The CaO values (Fig. 5A) are generally higher in the sandstone-dominated unit, reflecting the common occurrence of carbonate cements. Lower values of CaO reflect lower carbonate content associated with the siltstone facies and the variable weathering that occurs in the sandstone.

The MnO values are consistently higher in the sandstone-dominated unit and show no obvious differences among rock types within this unit (Fig. 5B). This trend is interpreted to indicate a difference in the paleo-oxygen levels under which the sandstone-dominated unit was deposited and may indicate either an influx of oxygen-rich water as the turbidity flows moved downslope into more anoxic, deeper waters or that there was a relatively abrupt change in the deep-basin redox conditions. The latter hypothesis seems more plausible because the hemipelagic mud and silt within the sandstone-dominated unit do not show decreased levels of MnO as would be expected if oxygen-rich waters were only periodically introduced by turbidite flows. The increase in relative abundance of coarse-grained lithotypes within the sandstone-dominated unit also indicates some change in paleoenvironmental conditions in this part of the basin.

Organic carbon (C org) (Fig. 6A) values are somewhat variable; however, the highest value (sample JC000131) occurs in a siltstone sample near the contact with the carbonaceous shale and siltstone-dominated units. Total carbon (Fig. 6B) is variable within the unit, but displays positive correlation with the sandstone samples and CaO (Fig. 5A) reflecting the increase in C with $CaCO_3$ content. The sulphur content (Fig. 6C) is typically low within the unit, but increases (in the siltstone samples) towards the lower part of the section reflecting increased sulphide mineralization in all the fine-grained lithotypes throughout the section relative to the coarser grained lithotypes. A weak positive correlation of

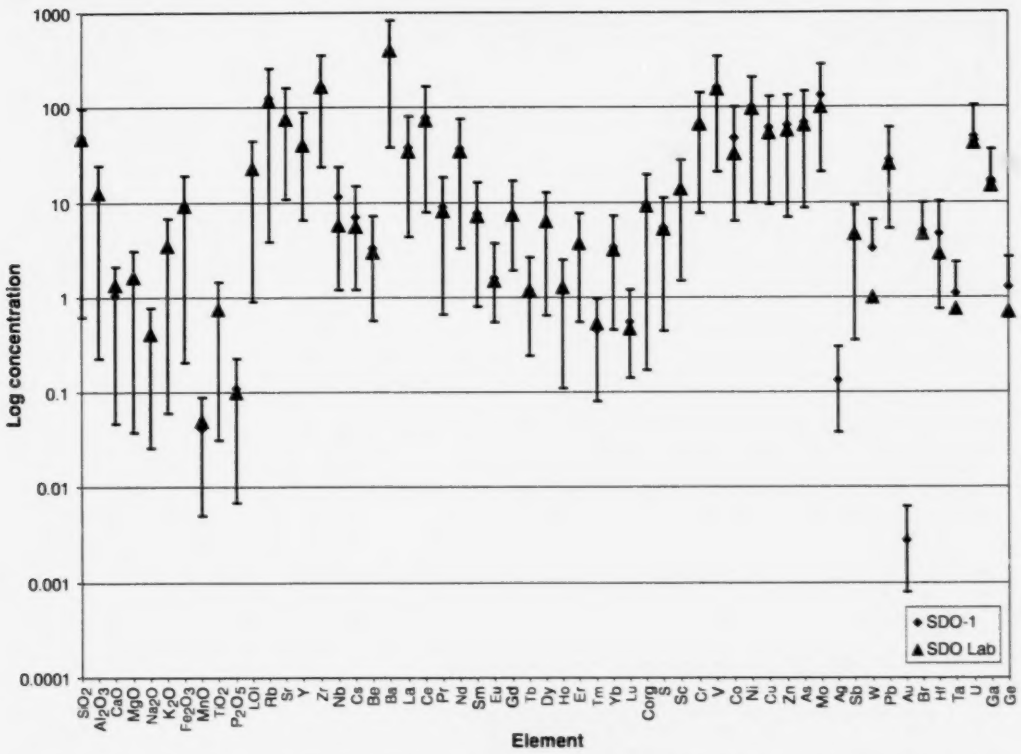
1000
100
10
1
0.1
0.01
0.001
0.0001
Log concentration
SDO-1
SDO Lab
SiO2 Al2O3 CaO MgO Na2O K2O Fe2O3 MnO TiO2 P2O5 LOI Rb Sr Y Zr Nb Cs Be Ba La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Corg S Sc Cr V Co Ni Cu Zn As Mo Ag Sb W Pb Au Bi Hf Ta U Ga Ge
Element

Figure 4. *Laboratory analysis of United States Geological Survey reference standard SDO-1 (black triangles) plotted on United States Geological Survey recommended ranges for standard SDO-1 (black diamonds with upper and lower limit bars). See text for usage.*

S with organic carbon also suggests that at least some of the sulphide is formed via bacterial sulphate reduction in association with organic carbon.

The transition metal content (Fig. 7) across the unit shows moderate positive correlation with organic carbon and S suggesting that the metals Cu, Zn, Ni, Co, V, and Th are associated with sulphide phases that are more prevalent in the finer grained rocks. The exception is Cr (Fig. 7B) which positively correlates with both CaO and total C and negatively correlates with S indicating that Cr is associated with detrital chromium-bearing species in the coarser grained sandstone facies. The concentrations of As, Pb (Fig. 7A), and U (Fig. 7C) show little variation across the unit and are in very low concentration, typically less than 10 ppm.

Siltstone-dominated unit

All facies of the siltstone-dominated unit show consistently low values of CaO (Fig. 5A) as compared to the sandstone-dominated unit, reflecting the relative absence of carbonate cement in all the mudrock facies within the Grog Brook Group. One sandstone sample (JC000146) is abnormally low in CaO because of weathering associated with the development of a pervasive cleavage near a north-striking fault.

The MnO content (Fig. 5B) is very consistent across the unit and, for the above reasons, is markedly lower compared to the sandstone-dominated unit. Organic carbon is more consistent and is slightly higher within the unit when compared to the sandstone-dominated unit (Fig. 6A). Total carbon is also more consistent and more closely follows the organic carbon values across the unit when compared to the sandstone-dominated unit (Fig. 6A, B), a feature associated with the low carbonate content in the siltstone-dominated unit. The S content (Fig. 6C) is consistently higher across the unit and correlates positively with both organic carbon and total carbon, again suggesting that some proportion of the sulphide is bacteriogenic.

The transition metals Cu, Zn, V, and Ni (Fig. 7) show a weak positive correlation with organic carbon, total carbon, and S indicating that these metals are concentrated in sulphide phases associated with carbon. Chromium is more consistent in the siltstone-dominated unit and shows no variation with organic carbon, total carbon, or S, again implying that the Cr is associated with detrital phases. The Cr concentrations in the siltstone-dominated unit are consistent with concentrations seen in the siltstone of the sandstone-dominated unit. The As and Pb contents are more difficult to assess due to low concentrations. Sample JC000146 is anomalous in that the concentrations of Cu, Zn, V, Co, Ni, and Cr are depleted

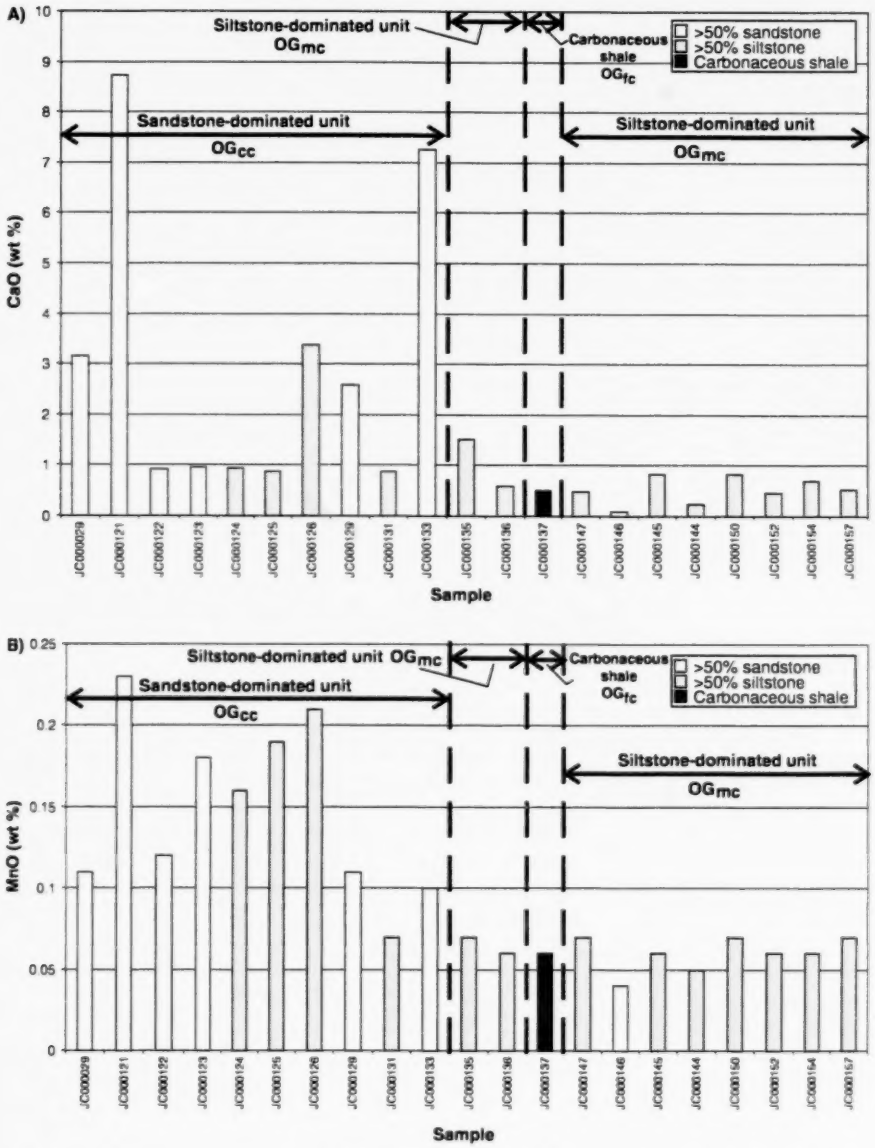

Figure 5. *Histogram plots of* ***A)*** *calcium oxide and* ***B)*** *manganese oxide along the Ritchie Brook transect. Left to right in the figure is west to east in the field. Dashed vertical lines indicate unit boundaries. See Figure 3 for the location of samples along Ritchie Brook.* OG_{mc}*=siltstone-dominated unit,* OG_{fc}*=carbonaceous shale unit,* OG_{cc}*= sandstone-dominated unit.*

relative to the rest of the unit. The best explanation for the low values is the removal of significant amounts of sulphide minerals by weathering of the sample. Interestingly, Cr also shows a small negative anomaly that would not be expected if all the Cr was associated with resistive detrital phases. Some of the Cr may be associated with sulphide phases or with less resistive silicate phases.

Thorium values, though variable, are locally twice as high as the average value across the unit (Fig. 7C). The reason for this trend is not readily apparent although both anomalously high samples (JC000146 and JC000144) are located near the fault and have strong deformation associated with them. It is possible that Th may have been introduced along the fault. The thorium content may also be associated with the slight increase in organic carbon in the unit since various carbon compounds are known to concentrate thorium (Parnell,

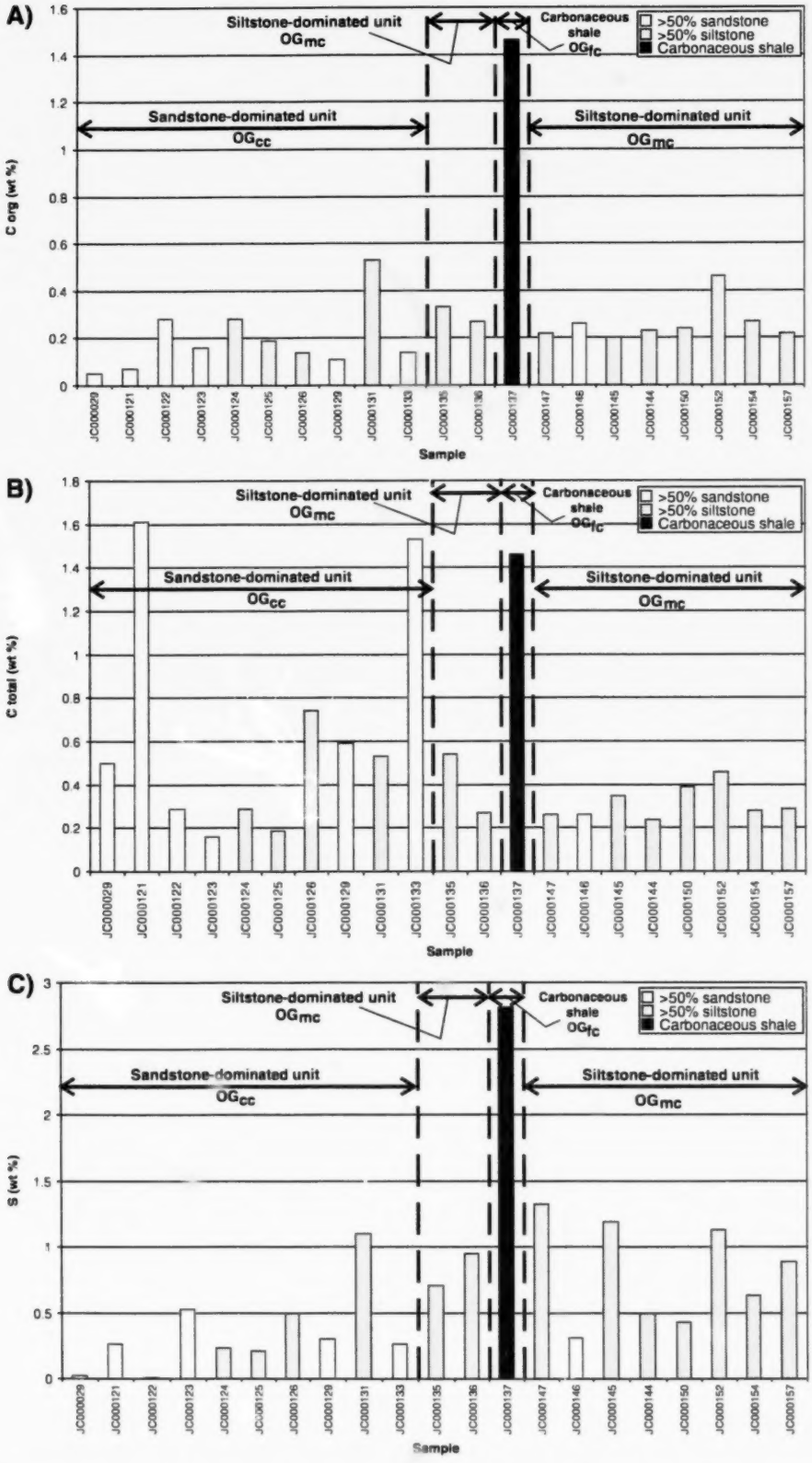

Figure 6.

Histogram plots of ***A)*** *organic carbon (Corg),* ***B)*** *total carbon, and* ***C)*** *sulphur along the Ritchie Brook transect. OG_{mc}= siltstone-dominated unit, OG_{fc}=carbonaceous shale unit, OG_{cc}= sandstone-dominated unit.*

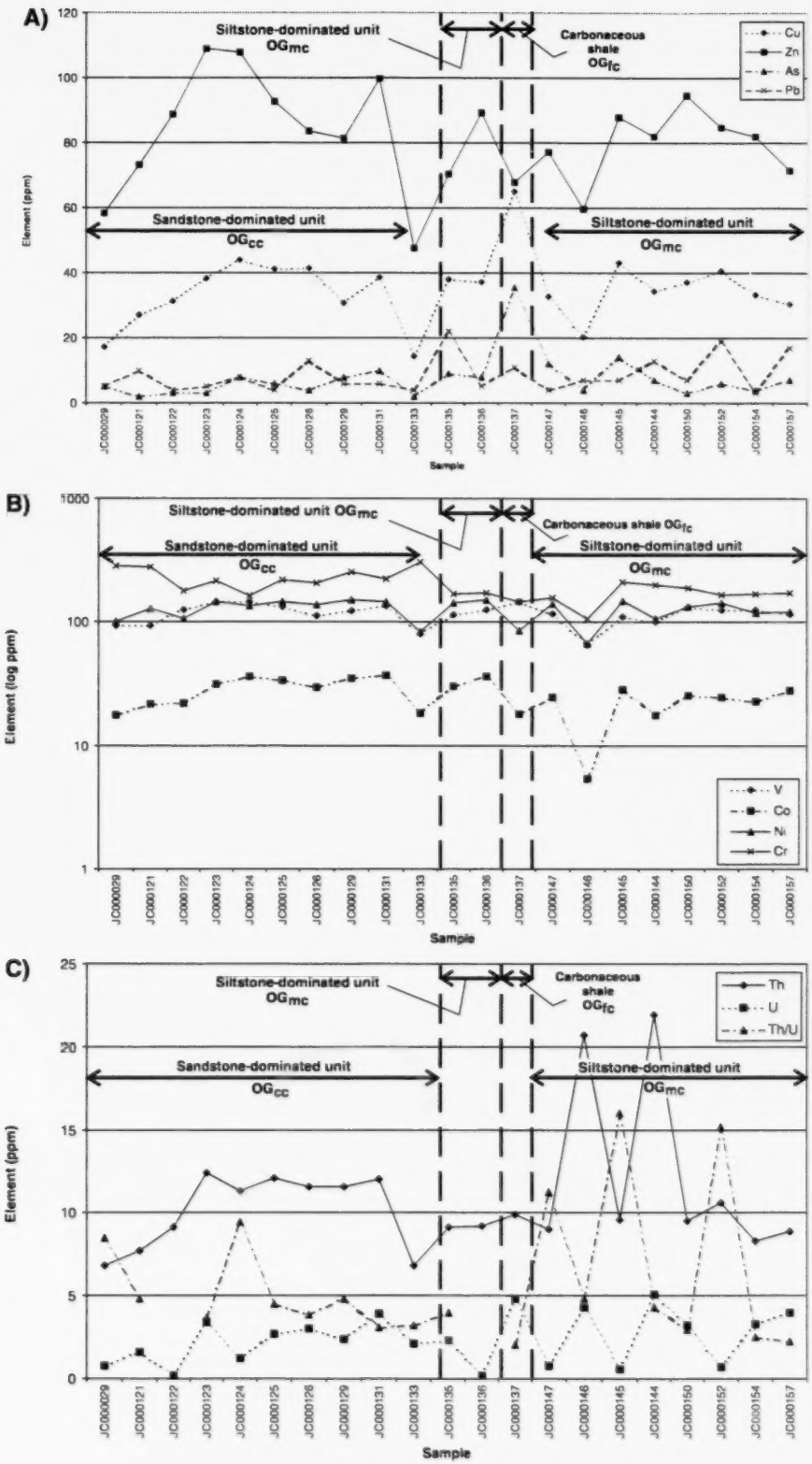

Figure 7.

Line plots of selected transition metals from west to east (left to right) along the Ritchie Brook transect: ***A)*** *variability of Cu, Zn, As, and Pb contents among the units;* ***B)*** *log plot of V, Co, Ni, and Cr; and* ***C)*** *normal plot of Th, U, and Th/U.*

1988). The elevated Th content is also recorded in the radiometric data from the Restigouche multiparameter airborne survey (Geological Survey of Canada, 1998b, Plates 98-2E and 98-2F; Carroll, 2000) in which the siltstone-dominated unit is mappable via the equivalent U and equivalent Th maps. Presumably, the finer grain size and greater density of the unit contribute to this phenomenon. The U values throughout the section are very low, typically less than 5 ppm, making definitive conclusions difficult; however, the Th/U values are higher on average in the siltstone-dominated unit.

Carbonaceous shale unit

Only one sample of the 'type' carbonaceous shale unit was obtained along the transect precluding any meaningful statistical evaluation; however, due to the field consistency of the unit as observed elsewhere and its unique character, some useful information may be obtained from the single sample.

The major oxide content (CaO and MnO, Fig. 5) is virtually indistinguishable from that of the siltstone-dominated unit suggesting that the redox conditions under which the unit was deposited, as well as possibly its provenance, were similar to those during deposition of the siltstone-dominated unit. The most significant deviation from the other units occurs with respect to the C and S contents (Fig. 6). The organic carbon content of the unit approaches 1.5%, at least three times greater than that of any other sample in the transect and the total carbon is virtually all organic. The S content in the carbonaceous shale sample is nearly twice that of any other sample and reflects the increased pyrite content relative to the other units (Fig. 6C). Clearly, the basin experienced some paleoenvironmental change at this point.

The preservation of organic matter in black shale is the subject of considerable debate (Wignall, 1994). On one hand, it may be argued that anoxic conditions are required to generate the conditions favourable for the preservation of significant amounts of organic matter. Conversely, it may also be argued that unusually intense biological productivity increases the amount of C that reaches the ocean floor irrespective of the redox conditions in the basin, although a large C flux into a basin could create internal anoxic conditions (Wignall, 1994). A debate on the validity of the 'preservation' model versus the 'productivity' model is beyond the scope of this paper, but either the redox conditions, the productivity, or some combination of both changed within the basin at the time of deposition. Both upper and lower contacts are gradational over as much as 100 m, suggesting that the change was at least relatively gradual. Conditions were probably more uniform for a longer period of time leading up to the deposition of the carbonaceous shale as evidenced by the more common occurrence of carbonaceous layers throughout the entire lower siltstone-dominated unit.

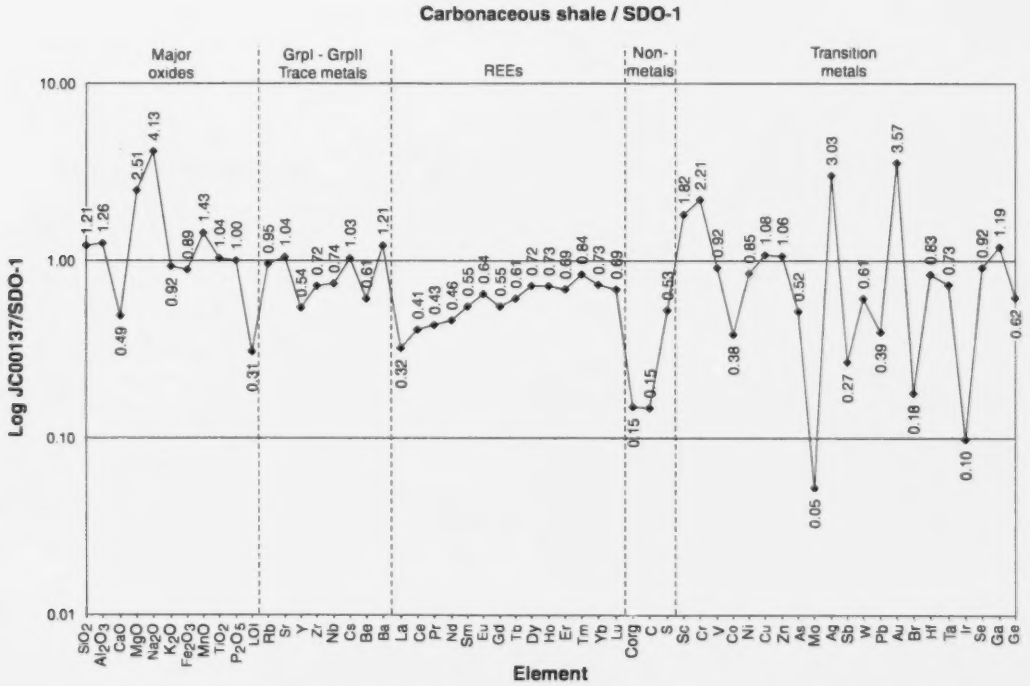
Carbonaceous shale / SDO-1
Major oxides
Grpl - Grpll Trace metals
REEs
Non-metals
Transition metals
Log JC00137/SDO-1
10.00
1.00
0.10
0.01
Element
SiO2 Al2O3 CaO MgO Na2O K2O Fe2O3 MnO TiO2 P2O5 LOI Rb Sr Y Zr Nb Cs Be Ba La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Corg C S Sc Cr V Co Ni Cu Zn As Mo Ag Sb W Pb Au Br Hf Ta Ir Se Ga Ge

Figure 8. *Element concentrations in sample JC00137 (carbonaceous shale) normalized to the average recommended values for United States Geological Survey geochemical reference standard SDO-1. Note that Cr, Ag, and Au contents are twice that of the standard. See text for explanation. Grp=group, Corg=organic carbon*

The transition metal content of the shale is of great interest. Only Cu and As are appreciably enriched, with V only very slightly enriched relative to the surrounding units, and Co, Ni, and Cr are depressed relative to the other samples (Fig. 7B). Carbonaceous material is well known for its ability to concentrate transition metals and it is somewhat surprising to see only limited enrichment of these metals within the unit. The best explanation for the low metal concentration is a lack of appreciable quantities of these metals at the time of deposition and diagenesis. There is also no field evidence for a hydrothermal component in the sediments or any appreciable degree of alteration.

A first attempt is made to characterize this shale relative to a recognized standard. Huyck (1991) proposed a definition of a 'metalliferous black shale' as being "a black shale that is enriched in any given metal by a factor of 2X (except for beryllium, cobalt, molybdenum, and uranium, for which 1X is sufficient) relative to the U.S. Geological Survey Standard SDO-1." The reasons for using standard SDO-1 include its well documented location and stratigraphic position in addition to its well constrained chemistry. Standard SDO-1 also qualifies as a black shale, having more than 0.5 % organic carbon. In addition, the definition does not render previous shale characterizations as obsolete (Huyck, 1991). Figure 8 illustrates the various elemental concentrations of sample JC000137 (carbonaceous shale unit) normalized to the recommended values for United States Geological Survey standard SDO-1. The sample is depleted in CaO and enriched in MgO and Na_2O relative to standard SDO-1, reflecting a higher degree of detrital input and a more mafic provenance of the sample. When compared to the standard, group I and II trace metals are similar whereas the REEs are all depleted, especially with respect to the LREEs. The transition metal content is largely similar to, or depleted with respect to the standard. The exceptions are Cr, Ag, and Au, which are enriched by factors of 2.21, 3.03, and 3.57, respectively, and thus, by the above definition, the carbonaceous shale sample (JC000137) is only considered to be a weakly 'metalliferous black shale'.

CONCLUSIONS

The sedimentary rocks of the Ordovician Grog Brook Group can be distinguished on a limited basis using major- and trace-element geochemistry. The Mn content can also help to elucidate some of the paleoenvironmental conditions under which the units were deposited. Manganese is soluble under reducing conditions, which implies that the environment, at least within the sediment pile, was reducing during deposition of the lower two units. Redox conditions during deposition of the sandstone-dominated unit are less clear because the Mn-bearing species is unknown. If Mn occurs as oxyhydroxides, oxidizing conditions are implied; if the Mn occurs as carbonate, reducing conditions are likely. No statement on the redox conditions of the water column can be inferred from this work.

The trace-element geochemistry is somewhat variable in all the units sampled and in the case of U, As, Pb, and Co, are in very low concentration and preclude their reliable use for discrimination between the three units. While the carbonaceous shale can be considered a weakly 'metalliferous black shale', it is not the source of the Ni-Co anomalies. Indeed, no obvious sources of either Ni or Co are present anywhere along the transect; this combined with the presence of the 'deep source' magnetic anomalies likely implies a source at depth.

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Geological Survey of Canada Project 990001ML

APPENDIX 1

Sample locations and results of analysis 1. Major oxides and C are in weight per cent, trace and elements are in parts per million except for Au which is in parts per billion. N/A is for not analyzed and 'bd' is below detection limit.

Sample	JC000029	JC000121	JC000122	JC000123	JC000124	JC000125	JC000126	JC000129
Latitude	47°39'51.79"N	47°39'58.40"N	47°39'58.54"N	47°40'01.27"N	47°40'11.92"N	47°40'13.79"N	47°40'13.85"N	47°40'01.31"N
Longitude	67°10'20.76"W	67°09'40.39"W	67°09'29.02"W	67°09'19.82"W	67°09'09.18"W	67°08'58.13"W	67°08'29.73"W	67°07'51.67"W
SiO_2	64.1	51	58.4	56.7	56.9	55.9	54.5	56.2
Al_2O_3	13.1	14.3	15.4	17.5	17.6	18	16.6	15.4
CaO	3.15	8.72	0.93	0.96	0.95	0.87	3.38	2.58
MgO	4.5	5.2	5.84	5.83	5.55	5.88	5.62	5.89
Na_2O	3.24	2.97	1.87	1.52	1.38	1.51	1.47	2.28
K_2O	1.36	1.61	2.81	3.19	3.26	3.25	2.87	2.52
Fe_2O_3	5.46	6.78	7.84	8.44	8.55	8.73	8.24	7.58
MnO	0.11	0.23	0.12	0.18	0.16	0.19	0.21	0.11
TiO_2	0.692	0.764	0.751	0.825	0.78	0.861	0.731	0.793
P_2O_5	0.15	0.27	0.14	0.15	0.17	0.14	0.14	0.14
Cr_2O_3	0.05	0.04	0.03	0.03	0.03	0.03	0.03	0.06
LOI	4.2	8	4.45	4.75	4.7	4.75	6.2	5.45
Total	100.1	99.9	99.6	100.1	100.1	100.1	100	99
Rb	25	53	59	79	99	134	78	65
Sr	187	337	106	86.9	92.1	82.3	149	177
Y	15.3	18.9	16.9	19.6	17.4	15.8	15.3	16.1
Zr	75.8	88	101	113	107	100	84.9	96.3
Nb	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Cs	0.6	2	5	3.9	6.7	6.6	4.2	3.5
Be	1.2	2.4	2	2.2	2.2	1.9	1.9	2
Ba	352	297	347	378	421	346	310	417
La	28.5	37.4	30.2	34.5	29.5	27.7	42.2	34.1
Ce	68	76	69	90	69	75	93	97
Pr	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Nd	30	27	49	51	31	30	46	23
Sm	4.83	6.56	5.51	6.07	4.99	5.02	6.07	5.92
Eu	2.18	2.52	1.75	1.74	2.22	1.17	2.09	1.61
Gd	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Tb	0.5	0.5	1.5	1.3	0.8	0.9	3.2	0.2
Dy	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Ho	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Er	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Tm	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Yb	2.22	2.52	2.39	2.72	2.85	2.96	2.49	2.59
Lu	0.45	0.38	0.44	0.51	0.35	0.51	0.2	0.19
Corg	0.05	0.07	0.28	0.16	0.28	0.19	0.14	0.11
C	0.5	1.61	0.29	0.16	0.29	0.19	0.74	0.59
S	0.02	0.26	0.01	0.53	0.23	0.21	0.5	0.3
Al	5.73	6.49	7.43	8.43	8.47	7.54	7.11	6.71
Ca	1.74	5.07	0.53	0.58	0.57	0.46	1.85	1.45
Mg	2.11	2.64	3.11	3.34	3.16	2.93	2.85	2.94
Na	1.98	1.9	1.17	1.04	0.94	0.89	0.9	1.37
K	1.1	1.3	2.1	2.72	2.79	2.31	2.18	1.78
Fe	3.56	4.44	5.22	6.33	6.55	6.55	5.9	5.16
Mn	645	1370	758	1160	1070	1070	1200	645
Ti	0.34	0.39	0.39	0.46	0.44	0.41	0.35	0.39
P	0.06	0.11	0.06	0.06	0.07	0.05	0.05	0.05
Sc	14.4	15.9	19.4	23.5	23.5	24.1	20.2	21
Cr	284	281	180	216	163	220	209	258
V	93	93	125	145	147	132	112	123
Co	17.5	21.7	22	31.2	36.1	33.7	29.8	34.8
Ni	101	129	107	145	136	147	138	152
Cu	17.2	27.1	31.2	38.4	44	41.1	41.3	30.7
Zn	58.3	73.1	88.8	109	108	92.8	83.7	81.4
As	5	2	3	3	8	6	4	8
Mo	bd	1	bd	bd	bd	bd	bd	bd
Ag	0.3	bd	0.3	0.4	0.6	0.6	0.4	0.3
Sb	0.7	0.4	0.2	0.9	0.5	1.3	2	1.6
W	5	5	4	12	7	2	1	3
Pb	5	10	4	5	8	4	13	6
Au	4	5	bd	bd	8	bd	4	2
Br	0.7	bd	bd	1.5	0.6	0.5	bd	bd
Hf	8.6	8.3	7.5	8	7.2	3.7	3.7	3.3
Ta	1.9	1.7	1.9	1.6	1.2	1.3	1.6	bd
Ir	10	12	11	10	bd	24	8	10
Hg	bd	1	2	bd	bd	1	bd	2
Th	6.8	7.7	9.1	12.4	11.3	12.1	11.5	11.6
U	0.8	1.6	0.2	3.4	1.2	2.7	3	2.4
Se	bd	2	4	2	4	bd	3	7
Tl	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Ga	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Ge	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
In	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

APPENDIX 1 (cont.)

Sample Latitude Longitude	JC000131 47°39'57.74"N 67°07'39.43"W	JC000133 47°39'57.44"N 67°07'15.32"W	JC000135 47°39'50.41"N 67°07'03.39"W	JC000136 47°39'49.81"N 67°06'52.24"W	JC000137 47°39'46.91"N 67°06'39.63"W	JC000147 47°39'20.35"N 67°04'48.40"W	JC000146 47°39'21.52"N 67°04'54.69"W	JC000145 47°39'28.65"N 67°04'52.85"W
SiO_2	56.7	60.9	63.1	61.5	59.7	60.5	66.7	56.6
Al_2O_3	17.6	11.5	13.8	15.5	15.4	15.7	15	16.8
CaO	0.87	7.26	1.51	0.6	0.51	0.48	0.09	0.84
MgO	5.5	3.55	5.24	5.3	3.86	5.35	4.53	5.58
Na_2O	1.43	3.32	2.3	1.86	1.57	2.53	1.5	2.51
K_2O	3.53	1.42	1.78	2.45	3.09	2.18	2.75	2.51
Fe_2O_3	7.83	4.44	6.71	7.3	8.28	7.36	5.18	8.13
MnO	0.07	0.1	0.07	0.06	0.06	0.07	0.04	0.06
TiO_2	0.873	0.605	0.66	0.736	0.737	0.756	0.477	0.853
P_2O_5	0.17	0.14	0.11	0.11	0.11	0.15	0.09	0.15
Cr_2O_3	0.03	0.04	0.03	0.03	0.02	0.03	0.02	0.04
LOI	5.15	6.55	4.75	4.65	6.7	4.8	3.8	5.35
Total	99.8	99.8	100.1	100.1	100.1	100	100.1	99.4
Rb	143	45	103	75	120	46	156	72
Sr	71.2	375	153	92	78	148	64.6	124
Y	16.1	14.8	14.9	16	22	11	25	15.9
Zr	107	69.7	83.7	86.9	118	84.4	91.9	81.7
Nb	N/A	N/A	N/A	N/A	8.4	N/A	N/A	N/A
Cs	3.4	2.8	2.9	0.9	7.1	6.5	10.2	6
Be	2.2	1	1.6	1.8	2	1.6	3	1.7
Ba	376	423	297	341	482	366	396	330
La	27.6	25.4	16.5	48.7	12.3	27.1	30.8	39.7
Ce	64	71	36	83	32.5	70	102	84
Pr	N/A	N/A	N/A	N/A	3.84	N/A	N/A	N/A
Nd	21	39	28	8	16.9	22	19	15
Sm	5.59	5.33	4.46	6.1	4.21	4.72	7.35	6.51
Eu	1.44	2.38	1.23	2.34	1.03	0.66	1.43	0.44
Gd	N/A	N/A	N/A	N/A	4.04	N/A	N/A	N/A
Tb	1.9	0.2	0.7	0.7	0.73	0.8	1.6	0.8
Dy	N/A	N/A	N/A	N/A	4.29	N/A	N/A	N/A
Ho	N/A	N/A	N/A	N/A	0.87	N/A	N/A	N/A
Er	N/A	N/A	N/A	N/A	2.49	N/A	N/A	N/A
Tm	N/A	N/A	N/A	N/A	0.376	N/A	N/A	N/A
Yb	3.38	2.62	2.26	2.19	2.48	2.16	4.49	2.19
Lu	0.31	0.43	0.3	0.5	0.373	0.4	0.66	0.35
Corg	0.53	0.14	0.33	0.27	1.46	0.22	0.26	0.2
C	0.53	1.53	0.54	0.27	1.46	0.26	0.26	0.35
S	1.1	0.26	0.71	0.95	2.81	1.32	0.31	1.19
Al	7.72	5.1	6.32	6.94	7	6.82	5.95	6.73
Ca	0.49	4.28	0.88	0.33	0.29	0.25	0.04	0.42
Mg	2.94	1.7	2.67	2.71	2.07	2.65	2.09	2.56
Na	0.88	2.05	1.47	1.16	0.99	1.53	0.82	1.36
K	2.56	1.02	1.39	1.82	2.39	1.64	1.91	1.64
Fe	5.65	2.98	4.7	5.56	6.15	4.94	3.75	5.57
Mn	411	582	426	358	342	371	221	365
Ti	0.44	0.3	0.35	0.37	0.37	0.36	0.21	0.31
P	0.06	0.06	0.04	0.04	0.04	0.06	0.03	0.05
Sc	23.2	14.6	19.1	21	24	18.9	15.3	21.1
Cr	222	306	169	171	147	158	106	213
V	136	80	114	126	147	117	66	110
Co	36.7	18.3	30.4	36.6	18	24.8	5.4	28.7
Ni	146	83	144	152	85	140	67	149
Cu	38.7	14.3	38	37.1	65	32.7	20.4	43.2
Zn	99.8	47.5	70.4	89.3	68	77.1	59.8	87.9
As	10	2	9	8	35.4	12	4	14
Mo	1	bd	bd	bd	7	bd	bd	2
Ag	bd	0.3	0.2	0.4	0.4	bd	bd	Bd
Sb	0.4	0.6	1.6	0.7	1.2	1	1.5	9.1
W	3	5	bd	2	2	bd	1	2
Pb	6	4	22	5	11	4	7	7
Au	6	7	4	2	10	4	bd	bd
Br	bd	1.2	bd	bd	0.9	bd	bd	bd
Hf	4	9.7	2	10.7	3.9	5	5.2	4.9
Ta	0.7	0.9	1.8	4.8	0.8	1.1	2.8	3
Ir	6	10	12	bd	bd	bd	14	13
Hg	bd	bd	2	2	bd	bd	bd	bd
Th	12	6.8	9.1	9.2	9.9	9	20.7	9.6
U	3.9	2.1	2.3	0.2	4.8	0.8	4.3	0.6
Se	4	2	2	bd	4	bd	3	2
Tl	N/A	N/A	N/A	N/A	0.55	N/A	N/A	N/A
Ga	N/A	N/A	N/A	N/A	20	N/A	N/A	N/A
Ge	N/A	N/A	N/A	N/A	0.8	N/A	N/A	N/A
In	N/A	N/A	N/A	N/A	bd	N/A	N/A	N/A

APPENDIX 1 (cont.)

Sample	JC000144	JC000150	JC000152	JC000154	JC000157
Latitude	47°39'27.73"N	47°38'52.62"N	47°38'47.36"N	47°38'40.67"N	47°38'36.09"N
Longitude	67°05'05.92"W	67°03'46.67"W	67°03'36.61"W	67°03'29.62"W	67°03'02.37"W
SiO_2	62.8	57.5	59.7	59.3	59.1
Al_2O_3	15.5	16.7	16.4	16.4	16
CaO	0.25	0.83	0.45	0.7	0.53
MgO	4.92	5.55	5.34	5.23	5.49
Na_2O	1.79	2	2.23	1.65	2.36
K_2O	2.76	2.67	2.61	3	2.6
Fe_2O_3	6.16	7.77	7.38	7.14	7.6
MnO	0.05	0.07	0.06	0.06	0.07
TiO_2	0.693	0.821	0.737	0.79	0.803
P_2O_5	0.13	0.16	0.13	0.14	0.14
Cr_2O_3	0.03	0.04	0.03	0.03	0.03
LOI	4.15	5.45	5.1	4.7	4.8
Total	99.2	99.5	100.2	99.2	99.4
Rb	92	86	55	114	86
Sr	87.8	112	87.1	71	83.1
Y	30.6	16.4	15.1	16.8	12.5
Zr	125	102	93.8	98.8	92.8
Nb	N/A	N/A	N/A	N/A	N/A
Cs	2.2	5.1	8.4	1.4	5.5
Be	2.6	2	3.5	2	1.8
Ba	441	440	400	470	380
La	48.3	33.3	15.2	28.8	24.4
Ce	114	78	39	61	46
Pr	N/A	N/A	N/A	N/A	N/A
Nd	60	21	5	39	45
Sm	8.54	5.54	3.8	5.42	4.89
Eu	0.48	1.52	0.96	1.93	1.62
Gd	N/A	N/A	N/A	N/A	N/A
Tb	0.1	1.2	1.6	1.3	1.3
Dy	N/A	N/A	N/A	N/A	N/A
Ho	N/A	N/A	N/A	N/A	N/A
Er	N/A	N/A	N/A	N/A	N/A
Tm	N/A	N/A	N/A	N/A	N/A
Yb	4.23	2.38	2.32	2.27	2.19
Lu	0.6	0.31	0.32	0.41	0.41
Corg	0.23	0.24	0.48	0.27	0.22
C	0.24	0.39	0.46	0.28	0.29
S	0.5	0.43	1.13	0.63	0.89
Al	7.24	7.38	7.37	7.42	6.62
Ca	0.12	0.48	0.25	0.41	0.28
Mg	2.68	2.97	2.77	2.79	2.62
Na	1.17	1.31	1.4	1.04	1.35
K	2.16	2.01	1.93	2.24	1.77
Fe	4.39	5.34	4.95	4.96	5.09
Mn	329	427	350	357	394
Ti	0.36	0.41	0.37	0.4	0.35
P	0.05	0.06	0.05	0.06	0.05
Sc	18.3	19.7	19	18.7	18.9
Cr	198	188	166	169	171
V	101	132	125	126	117
Co	17.5	25.6	24.8	22.7	28
Ni	107	132	142	118	122
Cu	34.4	37.3	40.5	33.2	30.4
Zn	82.1	94.7	84.7	82	71.6
As	7	3	6	4	7
Mo	1	bd	4	bd	bd
Ag	bd	bd	bd	0.7	0.2
Sb	2.2	0.5	1.8	0.5	3.3
W	2	1	4	bd	5
Pb	13	7	19	3	17
Au	7	6	3	4	5
Br	1	1.3	bd	0.7	1
Hf	7.4	4.2	4	5	7.2
Ta	bd	4.4	1.4	bd	bd
Ir	28	21	6	9	7
Hg	bd	bd	bd	bd	2
Th	21.9	9.5	10.6	8.3	8.9
U	5.1	3.2	0.7	3.3	4
Se	3	bd	4	4	3
Tl	N/A	N/A	N/A	N/A	N/A
Ga	N/A	N/A	N/A	N/A	N/A
Ge	N/A	N/A	N/A	N/A	N/A
In	N/A	N/A	N/A	N/A	N/A